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14. ABSTRACT This report results from a contract tasking University of Rome as follows: Among the approaches to predicting surface recombination and oxidation there are three classes , from the simplest to the more fundamental: 1. empirical recombination rates, as obtained from experiments on single TPS materials, i.e., $\gamma = \gamma(T)$, where γ is the recombination probability, usually measured as a function of temperature, but that depends also on pressure. 2. Kinetic models, where recombinations (but also oxidation) are described through a series of kinetic steps (elementary reactions) among species present in the shock layer and the particular TPS material. 3. Ab-initio (semi-classical and Q-M.) calculations, whereby a single species atom or molecule trajectory is simulated and the gas interface is reproduced as an atomic layer. Each class of models has many variants: for instance, kinetic models may use experimental data for the rates corresponding to each step, or deduce them from the surface potentials of each atom, as approximated in various ways; ab-initio calculations may rely on potentials surfaces obtained from Q.M. and using the Born-Oppenheimer approximation, or others; and so on: currently, the family tree of recombination has grown to a respectable size. Hence the need for examining in some detail each class of models, to gauge their range of applicability, complexity of use (for instance, in aerothermal CFD codes), and potential for future development. Some of these issues have been in fact explored by this writer for an ESA TRP project, yielding valuable insights as to the future of efficient modeling.					
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Kinetic catalysis model for silica surface: chemical energy accommodation

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1 ABSTRACT

This report addresses the problem of modeling Chemical Energy Accommodation (CEA) in the catalytic recombination of atomic species over the TPS of a re-entering spacecraft. CEA is the physical effect whereby energy released by the catalytic recombination of atoms such as O and N is transferred to the surface. This accommodation takes place during the desorption of reaction products. Often, the energy transferred is a small percentage of the total energy of recombination, reducing considerably the surface thermal load. Knowing the percentage of the energy actually deposited on the surface of a TPS is very important in making them lighter and more effective. In this context the usual assumption of complete accommodation, made chiefly for sheer convenience, can overestimate the actual heat flux transferred to the wall.

A simplified expression of the chemical energy accommodation coefficient (β) has been introduced in the kinetic catalysis model by Bruno et al., including all the mechanisms involved in the recombination phenomenon and the resulting recombination coefficient has been compared with the [few] experimental data available in the literature.

2 APPLICABILITY

- This report constitutes the last deliverable of EOARD Grant # 083024.

3 ACRONYMS AND SYMBOLS

CFD	Computational Fluid Dynamics
TPS	Thermal Protection System
E-R	Eley-Rideal recombination process
L-H	Langmuir-Hinshelwood recombination process
PR	Precursor Recombination mechanism
CEA	Chemical Energy Accommodation

Nomenclature

Latin Symbols

Y_i	mass fraction of i -th chemical specie
h	Planck constant
k	Boltzmann constant
j_i	specie i diffusion flux vector
m_i	molecular mass of species i
n_i	particle i number density
p	pressure
p_i	partial pressure
\dot{q}	thermal flux
NO	Nitrogen oxide
N_2	Molecular nitrogen
O	Atomic oxygen
O_2	Molecular oxygen

T	Temperature
s_a	atom sticking coefficient
s_m	molecule sticking coefficient
t	time
u	velocity component
v	velocity component
\bar{C}	mean particle velocity
D	dissociation energy
E	energy
E_m	adatoms migration energy
E_{X-Y}	chemical bond energy
G	free Gibbs energy
H	enthalpy
J_i	specie i total flux vector
$K_{w,i}$	wall catalyticity
L	intermolecular distance
P	steric factor
Q	activation energy
Q_a	adsorption energy
S	entropy
U_i	specie i diffusion velocity vector
V	flow velocity vector
Z	particle flux per unit area
Z_a	flux of atoms per unit area
Z_m	flux of molecules per unit area
Δh_i^0	formation enthalpy of i specie
D_{ij}	binary diffusion coefficient
D_{mj}	multi-diffusion coefficient
N	number of sites per unit surface
N'	number of adatoms moving per unit area

Greek Symbols

Δ	adjacent sites distance
ρ	density
β	chemical energy accommodation factor
γ	recombination coefficient
γ^*	microscopic Rideal recombination coefficient
θ	surface coverage
ν	hopping frequency

Subscripts

w	wall
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4 INTRODUCTION

During this final period of research the major effort was on improving and broadening the applicability of the kinetic model already discussed in the second Report. In particular, attention has been focused on the modeling of Chemical Energy Accommodation, i.e., transfer of chemical energy to the catalytic surface during the processes recombining atoms to form molecules.

The chemical energy coefficient, β , is defined as:

$$\beta = \frac{\text{heat flux released at surface}}{\text{heat flux of recombination}} = \frac{\dot{q}}{\frac{\Delta \dot{n}}{2} D} \quad (1)$$

where $\Delta \dot{n}$ is the number of atoms “consumed” by the unit surface in the unit time, so $\Delta \dot{n}/2$ is the flux of recombined molecules and D their dissociation energy.

If the molecule leaves the surface in an excited state only a fraction of its recombination energy would be deposited on the surface.

Some of the heterogeneous catalysis models found in the literature ([1], [2], [3], [4]), define recombination coefficients assuming full CEA ($\beta=1$). This approximation is used due to the complexity of the energy accommodation process and to the scant knowledge of the process itself.

In this case the atomic recombination coefficient γ coincides with the energy-transfer catalytic recombination coefficient, or effective recombination coefficient γ' , defined as:

$$\gamma' = \gamma \cdot \beta \quad (2)$$

The effective recombination coefficient is a very important quantity, since it defines the catalytic heat flux at a wall, not only as the result of the number of recombinations but also of the effective heat release to the surface by each recombination.

Scope of this work is thus to investigate the physics and the dependence of the chemical accommodation coefficient, in order to complete the kinetic model presented in the previous Report by deriving an expression of β capable of predicting partial accommodation.

To this purpose the starting point is the work of Halpern and Rosner [5], where they wrote a simple model for $\beta = f(T_w)$

These authors assumed that E-R forms excited molecules desorbing very fast (a gas/surface collision lasts for about a picosecond) so that molecules have very little time to exchange their excess internal energy with the surface. Accordingly, they predicted that the E-R mechanism will result in a very low CEA ($\beta < 1$). The L-H mechanism, instead, leads to an almost complete accommodation i.e., $\beta : 1$.

This trend has been recently supported by work by Cacciatore et al. [6], where semi-classical *ab initio* calculations of recombination of O atoms on SiO_2 surface show (for E-R recombination) that the energy deposited was very low, as molecules are predicted to desorb in a roto-vibrational excited state.

5 MODELLING CHEMICAL ENERGY ACCOMMODATION

Predicting the energy transferred to the surface by catalytic recombination is extremely complex. That is so not just quantitatively, but also because the dependence on all physical quantities is far from clear. Many experimental findings and calculations have shown that CEA is not related in a simple way to temperature, recombination mechanism, density of adsorbed atoms, and possibly on other factors. This is a case where the scientific community does not even know what are the unknowns.

This said, the aim is to identify at least some of the parameters that mainly influence the transferring of energy to the surface, and then to derive a simplified expression of the chemical accommodation coefficient, so as to improve our capability for numerically predicting the heat flux deposited on a TPS during re-entry.

What is, probably, less arbitrary and certainly useful for a first indication about β , is to estimate its minimum value, that corresponds to the case where recombined molecules desorb without depositing energy on the surface. This is the case where only adsorption is responsible for energy deposition, its adsorption energy transmitted to the solid on a time scale short compared to the other precesses.

This minimum value of β has been calculated by Halpern and Rosner [5] and is reported hereinafter, see equation (3)

$$\beta_{\min} = \frac{\frac{1}{2}Q_m\mu(1-\theta)^2 + Q_a(1-\theta) - Q_R\gamma^*\theta - \frac{1}{2}Q_{LH}\sigma\theta^2}{\gamma\frac{D}{2}} \quad (3)$$

where μ is the arrival rate, i.e. the ratio between molecular and atomic flux (Z_m/Z_a), γ^* is the microscopic Rideal recombination coefficient and σ is defined as:

$$\sigma = \nu n_i Z_m^{-1} \exp(-Q_{LH} / kT) \quad (4)$$

The first two terms in the numerator of equation (3) are the energies of molecules adsorption (dissociative adsorption) and atoms adsorption from which the energies needed for the activation of the two recombination processes (last two terms in the numerator) must be subtracted.

This expression has been modified in order to be compliant with the kinetic catalysis model developed by Bruno et al. and described in the previous Report of this contract [7]. In particular:

- the dissociative adsorption (molecules adsorption) is considered negligible with respect to the atomic one;
- the sticking coefficient s_a is different from 1, and has been introduced in the evaluation of the energy released by adsorbed atoms and in the total energy of recombination;
- desorption of atoms is considered as a further mechanism which “takes” energy from the surface that then must be added to the numerator of eq. (3);
- finally, the presence of OH surface contamination is modeled, with the result than some surface sites (modeled by a coverage θ_{OH}) are not free, that is not available for atoms adsorption.

Under these assumption the expression for β has been riformulated as follows:

$$\beta_{\min} = \frac{Q_a s_a (1 - \theta - \theta_{OH}) - Q_R \gamma^* \theta - \frac{1}{2} Q_{LH} \sigma \theta^2 - Q_a \delta \theta}{\left[s_a (1 - \theta) - \delta \theta + \gamma^* \theta \right] \frac{D}{2}} \quad (5)$$

This expression has been introduced in the kinetic model for a TPS based on an exposed silica surface, with the final recombination coefficient has defined by equation (2).

In Figure 1 β_{Omin} from equation (5) is plotted as a function of temperature, at various oxygen partial pressure, and in Figure 2 as a function of oxygen partial pressure and at various temperatures. Here the nitrogen partial pressure is kept constant.

β_{Omin} shows a monotonic increase with temperature; this is consistent with the idea that high accomodation levels are associated with L.-H. recombination and that this latter is enhanced as temperature increases.

Moreover, the distributions shown that β_{Omin} increases with increasing nitrogen partial pressure (p_N) and decreases with increasing oxygen partial pressure (p_O).

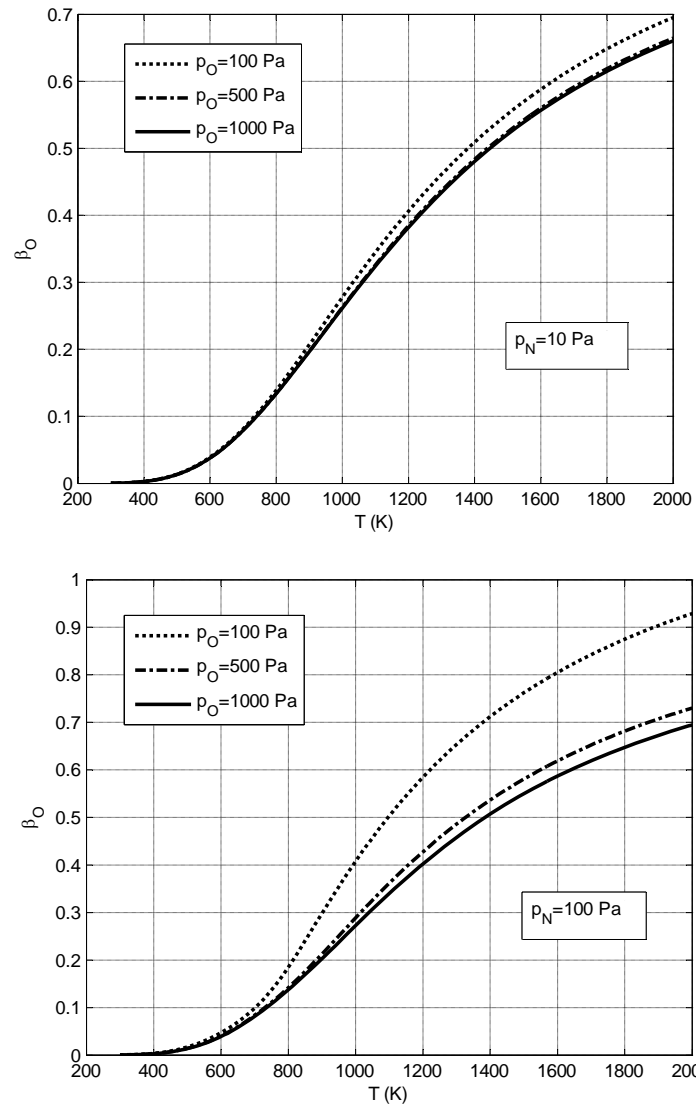


Figure 1. β_{min} as function of temperature; effect of oxygen partial pressure at fixed nitrogen partial pressure (top $p_{\text{N}} = 10$ Pa; bottom $p_{\text{N}} = 100$ Pa)

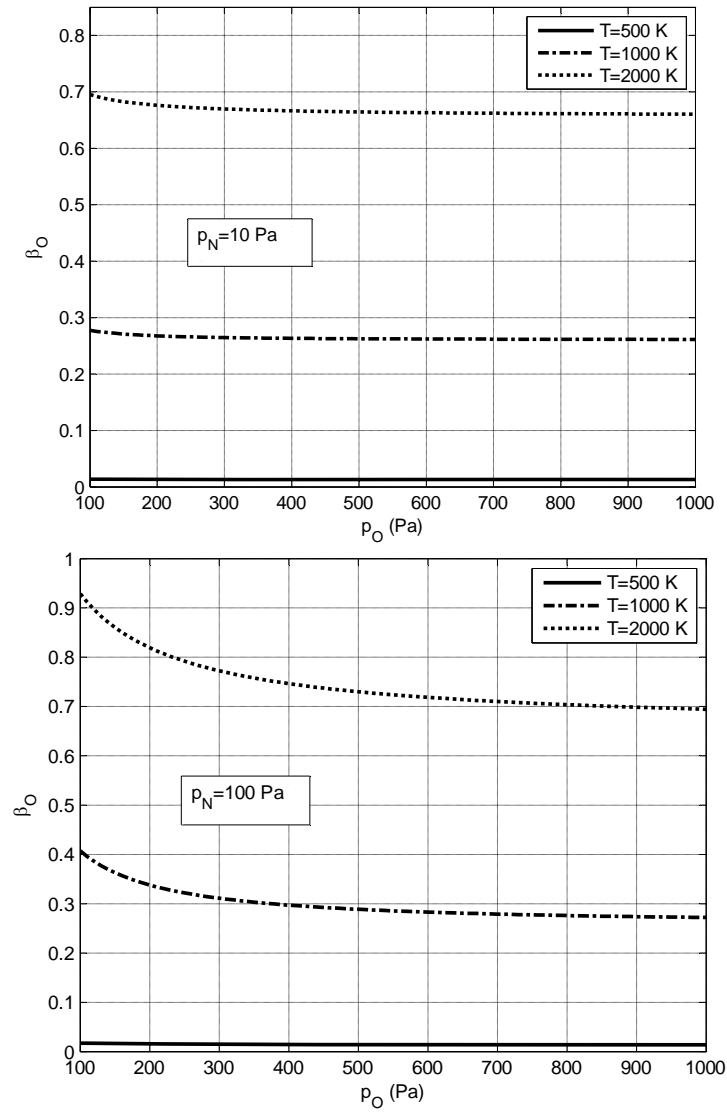


Figure 2. β_{\min} as function of oxygen partial pressure; effect of temperature at fixed nitrogen partial pressure (top $p_N=10$ Pa; bottom $p_N=100$ Pa)

6 VALIDATION TESTS

The new model including the effect of accommodation has been validated with the experimental data that could be found in the literature [8]. The data are constituted by experimental temperatures measured on the front surface of a SiC flat-faced cylinder in correspondence of two asymptotic conditions, indicated with FC-I and FC-II. The experiments were carried on in European facilities; in particular, the data reported here are those from the CIRA Plasma Wind Tunnel (“Scirocco”). The flows are characterized in terms of Pitot pressure and total enthalpy:

flow condition I (FC-I):

$P_{t2}=35$ hPa, $h_0=9$ MJ/kg

flow condition II (FC-II):

$P_{t2}=35$ hPa, $h_0=13$ MJ/kg

Figure 3 and Figure 4 show the comparison between *blind* CFD results and experimental measurements. Different catalytic conditions have been implemented. It is clear that the simplified assumption of non-catalytic (NC) or fully-catalytic (FC) wall lead to strongly under- or over-estimating the measured wall temperature, while the agreement obtained applying the kinetic model and shown in Figures 3 and 4 is surprising. Obviously, the new model with the effect of accommodation predicts lower temperatures, improving the agreement between CFD and measurements. As expected, the wall heat flux decreases due to accommodation, as shown in Figure 5 for the two FCs.

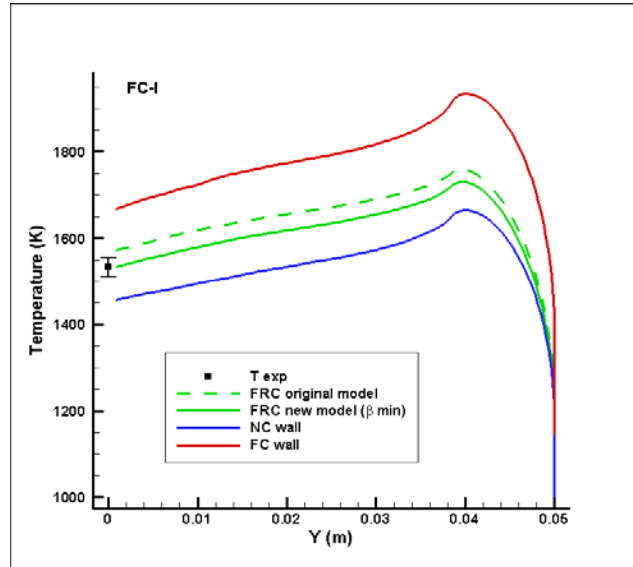


Figure 3. Flow condition FC-I, comparison between CFD and experimental result; effect of β_{\min}

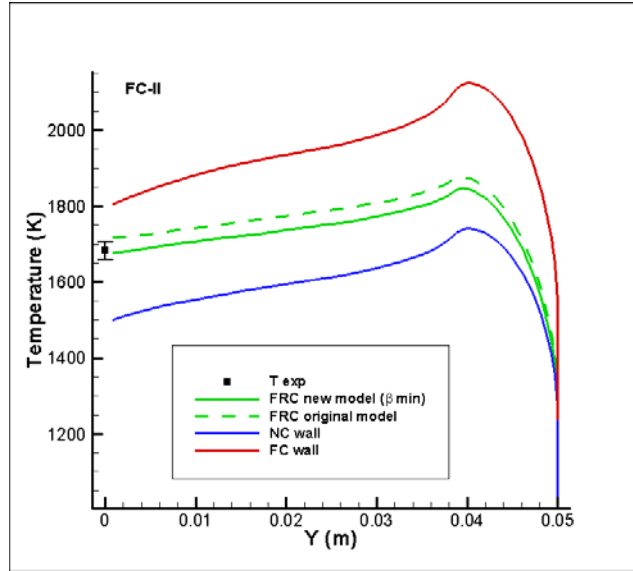


Figure 4. Flow condition FC-II, comparison between CFD and experimental result; effect of β_{\min}

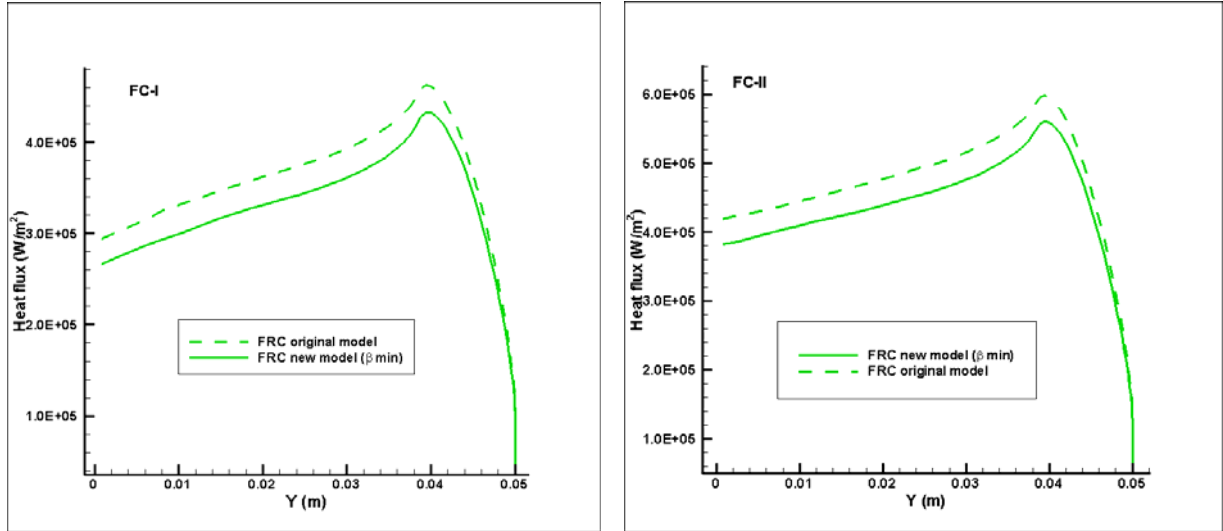


Figure 5. Flow condition FC-I and FC-II; effect of β_{\min} on heat flux

It is noteworthy that in the two cases presented the wall temperature is quite high and, as shown in Figure 1, β_{Omin} is also quite high. Therefore at these conditions the minimum value of β should be not much different from the actual one. Since in typical re-entry conditions, and for passive TPS, the surface temperature is close to that of radiative equilibrium, the error committed substituting β_{\min} for β is presumably not large, and the model presented above can be considered a good approximation.

7 DISCUSSION ON CEA

The chemical accommodation coefficient introduced in the kinetic model, is just a minimum value; in some circumstances the molecule just recombined can transfer to the surface an “extra” energy. The mechanisms which influence and favour this extra release of energy are still unclear; understanding these mechanisms is crucial to the final aim of the present research activity, that is, the capability of modelling them.

To this purpose much work has been done in order to identify the parameters that might have a role in the exchange of energy between gas and surface in catalytic processes.

Reading and comparing literature about CEA present in the literature (already cited in this Report and in the previous one) and looking at the physics of this phenomenon, three issues seem to us to play an important role in accommodation:

- the kinetic energy of the atom impacting the surface;

although this parameter has certainly an important role in the definition of β , as it is intuitive to think, the effect(s) due to accommodation when increasing the kinetic energy of the impacting atom is/are not clear. An in-depth analysis of this dependence is that by Cacciatore et al. [6]. Results of molecular dynamics show that increasing kinetic energy (increasing macroscopic temperature) generally leads to a higher transfer of energy to the surface, but, at the same time, the collisional regime reduces the probability an atom has to react: the tendency for an atom is to be trapped or to be scattered back to the gas phase. Thus there should be a point when chemical energy accommodation inverts its dependence on kinetic energy. Note that in the expression for the chemical energy accommodation formulated by Balat et al. [9] the velocity of the atom impacting the surface appears in the denominator.

- the lifetime of the molecule before desorption;

this point is commonly accepted: the increase of β in a recombination mechanism depends on the lifetime of the molecule formed before desorption. Halpern and Rosner [5] suggest that it is the time associated with the two recombination processes (E.-R and L.-H.) that ensures the higher release of energy to the surface in the case of L.-H. recombination (the slower between the two mechanisms).

- the coupling between the vibrational frequency of recombining molecule and the solid lattice;

at a surface, there are two main channels for energy deposition, namely phonons and electron-hole pair excitations. Phonons usually are understood to be the main channel for dissipation [10]. Our original idea is that if during the interaction between molecule and phonons there is coupling between molecule vibration frequency (characteristic interaction time) and surface vibration modes. Growing efficiency of this interaction (frequency matching) raises also the transfer of energy to the surface. Therefore one should know the phonon frequency distribution and compare it to the characteristic time of recombination of a molecule at the surface. This work is now in progress.

Once these three issues have been analyzed and recognized among as the main contributors to the possible increase of β with respect to the minimum defined by equation (5), the next step should be that of improving the modelling developed with the introduction of the following quantities: kinetic energy of impacting atom, interaction time, characteristic frequencies of the solid composing the outer TPS surface .

8 SYNTHESIS OF THE ACTIVITY SO FAR AND CONCLUSIONS

Original aims of this research activity were:

- the evaluation of the state of the art in catalytic recombination, both from the numerical and from the experimental point of view ;
- the detailed description of the kinetic catalysis model with application to silica surface and validation with experimental data;
- identification of missing physics and neglected effects;
- development of a new and more realistic model, and possible links with the results provided by molecular dynamics;
- modelling of chemical energy accommodation, introduction of the new parameter in the kinetic model, validation of the new model with literature data and evaluation of the improvement obtained with respect to the previous model;
- singling out possible ways to improve the new modelling.

In particular, in this Report simplified modelling of the chemical energy accommodation coefficient has been carried out with an approach based on its minimum value. Its expression, introduced in the kinetic model, allows the definition of the *effective recombination coefficient*, that includes the effect of catalytic recombination as the result of both the number of recombinations and of the heat release at the surface by each recombination.

The validation of the new model with the little available in the open literature shows very good agreement, and that introducing the β coefficient in the model predict more realistically the effect of catalysis on the heat flux of a surface exposed to a high energy flow.

Moreover, it has been shown that at high surface temperatures the value predicted by this new model is close to its maximum value, confirming that at high temperature L.-H. is the dominant recombination mechanism.

Finally, the many scientific aspects and issues (some forbidding) of this project has forced these investigators to go into very detailed physics of surfaces and interfaces. This work is not showing yet in the results presented here, mainly because of the limited grant time. However, its importance and actual results will be presented in the PhD thesis of one of us (S. Di Benedetto) that should become available in a year or so. Here at least the bases have been posed for future more accurate modelling of catalytic recombination in hypersonics.

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